

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 583 062 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
29.09.1999 Bulletin 1999/39

(51) Int Cl.⁶: **D01F 9/127, H01M 4/96**

(21) Application number: **93305272.2**

(22) Date of filing: **06.07.1993**

(54) **Graphitized carbon fibers**

Graphitisierte Kohlenstoffasern

Fibres de carbone graphitisées

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **06.07.1992 JP 17868792**

(43) Date of publication of application:
16.02.1994 Bulletin 1994/07

(73) Proprietor: **NIKKISO CO., LTD.**
Shibuya-ku Tokyo 150 (JP)

(72) Inventors:
• **Harada, Minoru,**
Halbara-gun, Shizuoka-ken (JP)
• **NiiYama, Masanori,**
Halbara-gun, Shizuoka-ken (JP)

(74) Representative: **Calamita, Roberto**
Frank B. Dehn & Co.,
European Patent Attorneys,
179 Queen Victoria Street
London EC4V 4EL (GB)

(56) References cited:
EP-A- 0 433 507 **US-A- 4 518 575**

- **JOURNAL OF APPLIED PHYSICS**, vol. 62, no. 9,
1st November 1987, pages 3947-4952, American
Institute of Physics, Argonne, IL, US; B.
**MARSHIK et al.: "Electron-spin-resonance
studies of vapor-grown carbon fibers"**

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

Not : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

D scripti n

[0001] The present invention relates to vapor-grown and graphitized carbon fibers, a process for the preparation of the carbon fibers grown in a vapor phase and then graphitized, molded members of the vapor-grown and graphitized carbon fibers, and composite members thereof. More particularly, the present invention relates to vapor-grown and graphitized carbon fibers suitable for composite members such as composite materials, composite molded members or the like, or molded members formed substantially solely with the vapor-grown and graphitized carbon fibers, a process for the preparation of the vapor-grown and graphitized carbon fibers, the molded members thereof comprising solely or substantially solely of the vapor-grown and graphitized carbon fibers, and composite members comprising the vapor-grown and graphitized carbon fibers and a matrix.

[0002] Carbon fibers grown in a vapor phase which may be designated as vapor-grown carbon fibers can be prepared by subjecting a carbon compound to heating at temperature ranging from 800°C to 1,300 °C in the presence of a catalyst comprising iron or nickel in the superfine particle form. The resulting vapor-grown carbon fibers then can readily be converted into the carbon fibers having a graphite structure by heating the vapor-grown carbon fibers. For example, when the vapor-grown carbon fibers are heated at temperature higher than 2,800°C to form vapor-grown and graphitized carbon fibers, the crystal lattice planes in the direction parallel to the fiber axis have less defects and can be compared to the annual growth rings of a tree. Hence the carbon fibers grown in the vapor phase and then graphitized have a high degree of physical strength and elastic modulus and are highly conductive thermally and electrically.

[0003] It is thus greatly expected that the vapor-grown and graphitized carbon fibers can provide composite materials having excellent properties. With this expectation, extensive review has been made with the attempt to develop molded members containing such vapor-grown and graphitized carbon fibers at a high packing density and consisting substantially solely of such carbon fibers.

[0004] As a result of such extensive review, however, it has been found difficult to form such molded members consisting substantially solely of such vapor-grown and graphitized carbon fibers and containing them at a high packing density. This difficulty may be assumed to reside in the matter that, when the vapor-grown and graphitized carbon fibers are mixed with another material to thereby form a composite material, there are employed the vapor-grown and graphitized carbon fibers that are prepared by adjusting the vapor-grown carbon fibers with a means such as a ball mill or the like so as to have an appropriate fiber length, for example, having an aspect ratio of 100 or lower in order to prevent the carbon fibers from uneven dispersion, and then by subjecting the resulting carbon fibers to graphitization. The vapor-grown and graphitized carbon fibers so prepared are less defective in crystalline structure so that they are less wettable with other materials and high in elastic modulus. Hence, the shape of a molded member formed from vapor-grown and graphitized carbon fibers cannot be sustained due to the high packing density. Further, the resulting molded members become very fragile even if the shapes of the vapor-grown and graphitized carbon fibers could be sustained.

[0005] On the other hand, extensive review has recently been made with the attempt to develop a lithium ion secondary battery that uses carbon as an active substance for an electrode.

[0006] Although a lithium secondary battery has drawn attention due to its high energy density, there is the risk that may occur if its electrode is not sealed in a complete way because a metallic lithium that is highly active to oxygen and moisture is employed for the electrode. Further, it can suffer from the disadvantage that the electrodes are short-circuited due to the formation of needle-like crystals of lithium, i.e. dendrite, on the surface of the lithium electrode. Hence, a growing interest has been shifted to the lithium ion secondary battery which uses as the electrode a carbon that can form an intercalation compound with the lithium ions, because the lithium ion secondary battery does not cause those risk and disadvantage, even if the lithium ion secondary battery should sacrifice the energy density so high as prevailing in the lithium secondary battery to some extent.

[0007] Among the carbon-lithium ion intercalation compounds, the compound that contains a largest amount of lithium ions is a compound of first stage and the ratio of carbon atoms to lithium atoms is six to one (6 : 1). If all the carbons are used for producing intercalation compounds and all the lithium atoms intercalated on a charging process are fully de-intercalated on the discharging, the quantity of electricity that can be discharged is a maximum of 372 mAh per gram of carbon. Although a variety of efforts have been made so far to attain the theoretical quantity of dischargeable electricity, however, no compound of first stage having a satisfactorily high quantity of electricity is found yet.

[0008] The primary object of the present invention is to provide vapor-grown and graphitized carbon fibers capable of formulating composite members such as composite materials consisting substantially of the vapor-grown and graphitized carbon fibers or composite molded members.

[0009] Another object of the present invention is to provide a process for the preparation of the vapor-grown and graphitized carbon fibers.

[0010] A further object of the present invention is to provide molded members having the vapor-grown and graphitized carbon fibers contained at a high packing density.

[0011] A still further object of the present invention is to provide composite members containing the vapor-grown

and graphitized carbon fibers.

[0012] In order to achieve the objects as described hereinabove, the present invention consists of the vapor-grown and graphitized carbon fibers as defined in appended claim 1.

[0013] The present invention further consists of the process for the preparation of the vapor-grown and graphitized carbon fibers, which is characterized by subjecting vapor-grown carbon fibers, which are not fractured to a substantial extent, to graphitization by heating them at temperature of 2,000°C or higher and then by fracturing the resulting vapor-grown and graphitized carbon fibers at a high impact so as for the resulting vapor-phase and graphitized carbon fibers to have a spin density of 8×10^{18} spins/g or less, when measured by the electron spin resonance absorption method.

[0014] The present invention additionally concerns molded members consisting substantially solely of the vapor-grown and graphitized carbon fibers.

[0015] Furthermore, the present invention concerns composite members comprising of the vapor-grown and graphitized carbon fibers and a matrix.

[0016] Figure 1 is a schematic representation showing the structure of an example of a high-impact treatment apparatus so adapted as to be employed appropriately for the process according to the present invention.

a. Vapor-Grown and Graphitized Carbon Fibers

[0017] Vapor-grown and graphitized carbon fibers may also be abbreviated to VGCF in this specification.

[0018] The VGCF according to the present invention have a mean fiber diameter of 5 μm or smaller, preferably from 0.1 μm to 3 μm , and more preferably from 0.3 μm to 2 μm ; a mean fiber length of 90 μm , or shorter, and a mean aspect ratio of from 1 to 18, preferably from 2 to 16, more preferably from 5 to 15. The VGCF having such characteristics can be used to form molded members and composite members with high packing density.

[0019] Alternatively, it is preferable that the VGCF have a mean fiber diameter of from 1.5 μm to 3.0 μm with a view to retaining a high charge volume of negative electrode in a secondary battery. When the mean fiber diameter of VGCF is smaller than 1.5 μm , the charge volume of the negative electrode in a secondary battery becomes small. When the mean fiber diameter of VGCF is larger than 3.0 μm , the shape of electrode becomes degraded and the electrode's cycle of charge and discharge characteristics are reduced.

[0020] When the mean aspect ratio of the VGCF exceeds 18, composite molded members having good properties cannot be prepared.

[0021] The VGCF according to the present invention have a spin density of 8×10^{18} spins/g or less, preferably 7×10^{18} spins/g or less, when measured by the electron spin resonance absorption method.

[0022] When the spin density of the VGCF according to the present invention is within the range described hereinabove, the resulting carbon fibers can be used to produce a coating layer or can be molded into an article which retains its shape and can also be used as a material having a high amount of discharge. Therefore the carbon fibers can be used as a battery electrode for use with intercalation compounds of the lithium ion.

[0023] The VGCF according to the present invention have an interplanar distance (d_{002}) of the graphite lattice which may be usually 3.45 Å or shorter, preferably from 3.35 Å to 3.42 Å, more preferably from 3.35 Å to 3.37 Å, and the thickness of the graphite lattice plane in the condensed benzene ring's form, that is, the thickness (L_c) of the laminated lattices in the crystal which may be usually 30 Å or thicker, preferably 300 Å or thicker, more preferably 1,000 Å or thicker, when considered from the point of view that highly developed graphitization contributes to form good retention of shape of molded members made by VGCF, good formation of intercalation compound made by VGCF and lithium, good formation of molded members having high electrical conduction, and good composite members forming thin layer and having large strength and highly conductive thermally and electrically.

[0024] The VGCF according to the present invention may be appropriately employed for the preparation of composite members, such as the composite materials and composite molded members. The composite materials may be prepared by compounding the VGCF with a plastic material, a rubbery material, a metallic material, a ceramic material, a paint or an adhesive, with a high packing density. The composite molded members consisting solely or substantially solely of the VGCF may be prepared by compounding a large quantity of the VGCF with the possible smallest amount of a binder, if necessary. The composite materials and the composite molded members may be used as highly electrically conductive materials, highly thermally conductive materials or carriers for catalysts.

b. Process for the Preparation of the VGCF

[0025] The VGCF according to the present invention, that is, the VGCF suitable for the composite materials, can be prepared by the procedures of the process according to the present invention as will be described hereinafter in more detail.

[0026] More specifically, the VGCF can be prepared by heating the vapor-grown carbon fibers at a temperature of, for example, 2,000°C or higher and thereby subjecting the vapor-grown carbon fibers to graphitization, followed by

fracturing the resulting vapor-grown and graphitized carbon fibers at a high impact. The vapor-grown and graphitized carbon fiber may be designated as pre-VGCF as distinct from VGCF of present invention because of the fracturing step.

[0027] The vapor-grown carbon fibers can be prepared by the vapor phase method as will be described hereinafter. The vapor phase method to be applied to the formation of the vapor-grown carbon fibers to be used for the present invention may include a so-called substrate method, i.e. the method for the growth of the carbon fibers on a substrate and a so-called fluidized growth method, i.e. the method for the growth of the carbon fibers in a flow. The substrate method involves flowing hydrocarbon gas as a carbon-source gas over a base with a catalyst metal such as a transition metal or a transition metal compound deposited thereon in a high temperature furnace, thereby depositing carbon fibers on the surface of the substrate. The fluidized growth method involves flowing a mixture of a metallic compound, serving as a catalyst metal, and a carbon compound, serving as a carbon source, in a vapor phase through a reactor tube heated at high temperature, without the use of any base, thereby forming carbon fibers in flowing gas in the reactor furnace.

[0028] Specifically, the vapor-grown carbon fibers to be used as a raw material for the process according to the present invention can be prepared by processes disclosed, for example, in Japanese Patent Unexamined Publication (kokai) Nos. 52-107,320, 57-117,622, 58-156,512, 58-180,615, 60-185,818, 60-224,815, 60-231,821, 61-132,600, 61-132,630, 61-132,663, 61-225,319, 61-225,322, 61-225,325, 61-225,327, 61-225,328, 61-227,425, and 61-282,427.

[0029] The vapor-grown carbon fibers to be employed for the process according to the present invention can then be treated by graphitization that involves heating them at temperature of approximately 2,000 °C or higher to thereby yield the pre-VGCF.

[0030] The graphitization may usually be carried out in an atmosphere in which an inert gas, for example nitrogen, helium or argon is present. The time required for the graphitization may be usually five minutes or longer.

[0031] In accordance with the process according to the present invention, the pre-VGCF prepared in the manner as described hereinabove are then treated by fracturing them at a high impact to form VGCF.

[0032] It can be noted that, generally, when the molded members and composite members are prepared from the VGCF, it is necessary that the pre-VGCF having their original length as grown after graphitization be fractured, because it is difficult to mix pre-VGCF with other components homogeneously. In this case, in order to allow the graphitization to be carried out in an efficient way, the pre-VGCF of the state of the art are usually fractured prior to the graphitization to reduce the bulkiness of the carbon fibers.

[0033] It has been found by the present inventors, however, that there is a great difference between the VGCF prepared by carrying out the fracture treatment prior to graphitization as in the conventional method and those prepared by carrying out the fracture treatment after the graphitization as in the present invention. The reason for creating that great difference is not yet clarified.

[0034] It is further found that, when the pre-VGCF are fractured at a high impact prior to the graphitization, the resulting VGCF has a high spin density at $g=2.015$ in the electron spin resonance (ESR). It can be noted herein that the g value of 2.015 corresponds to the oxygen radical.

[0035] On the other hand, it is found that, when the pre-VGCF are not caused to be fractured to a substantial extent prior to the graphitization and they are fractured at a high impact after the graphitization, as in the present invention, the spin density can be reduced, thereby improving the physical properties of the resulting molded members and composite members.

[0036] From the finding as described hereinabove, the process for the preparation of the VGCF according to the present invention comprises fracturing the pre-VGCF by applying the high impact thereto.

[0037] The methods for milling and crushing, such as with a ball mill or a roller mill, are generally adopted in order to make finely divided particles of materials further smaller. The ball mill, roll mill or such other procedures, however, may grind or crush the pre-VGCF to such an extent that a portion of the VGCF cannot sustain their fibrous shapes any more and it is difficult to control the ball mill, roll mill or such other procedures so as to make the fiber length a desired value. Further, these milling processes require a longer time for treatment.

[0038] On the other hand, it is preferred that the process according to the present invention is carried out by fracturing the pre-VGCF solely by applying the high impact thereto. The process according to the present invention can, within a treatment time as short as several minutes, conveniently adjust mean fiber length and so on, of the VGCF so as to have as defined by the present invention.

[0039] More specifically, an example of the treatment for fracturing the pre-VGCF involves applying the high impact to the pre-VGCF through the high-impact treatment apparatus as shown in the Figure. The high-impact treatment apparatus comprises a cylindrical container 3 having a plurality of impact blades 3 arranged radially so as to be rotatable and a self-circulation path 1 having its one end mounted to a peripheral side of the cylindrical container 3 and having the other end mounted to a central portion of a flat plate of the container 3 so as to form a passage for air flow. The high-impact treatment apparatus may allow the pre-VGCF to be placed therein and to apply the high impact to the pre-VGCF by rotating the impact blades 2 at a high speed.

[0040] The fiber length of the VGCF can be adjusted mainly by changing the power of the high impact in the treatment

by applying the high impact to the pre-VGCF. The high impact can be applied by rotating the impact blades of the high-impact treatment apparatus although it is also possible to strike the pre-VGCF to the blades or the inner peripheral wall of the cylindrical container in a one-way direction or in reciprocating directions. The rotation of the impact blades is preferred because it is easier in operation than the other procedures. The application of the high impact to the pre-VGCF allows the fibers to be cut or fractured at two occasions: at the first occasion when the fibers are caused to be struck to the impact blades and at the second occasion when they are caused to be struck to the inner peripheral wall of the container.

[0041] The conditions for applying the high impact to the pre-VGCF may vary greatly with the kind of the high-impact treatment apparatus. In other words, the various conditions can conveniently be chosen to thereby have the pre-VGCF ground or fractured so as to make the VGCF have a spin density of 8×10^{18} spins/g or less, when measured by the electron spin resonance absorption method.

[0042] Although the velocity of rotation of the impact blades applying the high impact to the pre-VGCF (or the velocity at which the pre-VGCF are struck to the inner peripheral wall of the container of the high-impact treatment apparatus) can appropriately be chosen in accordance with the desired fiber dimension or the desired aspect ratio, the velocity of the rotation of the impact blades may preferably be set to 40 meters per second, more preferably to 60 meters per second. The higher velocity can offer the better effect upon the fracture of the pre-VGCF. The operation of the apparatus at the velocity exceeding 100 meters per second may suffer from the disadvantages, however, that the apparatus should become larger in size due to the necessity of a protective device for safety measures, the way of operating the apparatus may become complex, and the operation may cause the economical inconvenience. The time required for the fracture of the pre-VGCF may appropriately be within 5 minutes and a longer treatment time is economically disadvantageous. It is to be noted herein that the velocity of the rotation of the rotatable impact blades is determined as the velocity at which their outermost ends of the impact blades rotate, because the velocity of the rotation at the outermost ends of the impact blades is the fastest and it can offer the greatest effect upon the fracture of the pre-VGCF.

[0043] The treatment by fracturing the pre-VGCF in the manner as described hereinabove can form the VGCF having the spin density of 8×10^{18} spins/g or less, when measured by the electron spin resonance absorption method.

[0044] Decreasing of the spin density means decreasing the amount of oxygen radical on the surface of VGCF.

[0045] Unclear is the reason why the amount of oxygen radical is decreased by the fracturing of pre-VGCF with high-impact and the amount of oxygen radical is not so decreased by the graphitizing vapor-grown carbon fibers and fracturing. The inventors suppose that graphitizing causes to arrange graphite structure to generate carbon radicals and those radicals react with air to form oxygen radicals after fracturing. Alternatively, it is supposed that generated oxygen radicals are changed to functional groups by fracturing. When graphitization is carried out after the fracturing, pyrolysis will decompose the functional groups generated.

[0046] It is supposed that the generated oxygen radicals exist mainly on the surface of fracturing section or cutting section through which lithium ion can enter VGCF in lithium secondary battery and therefrom the oxygen radicals react with the other compounds for example solvents to form solid electrolyte interface (SEI) which prevents lithium ion to enter VGCF. Alternatively, it is supposed that because the functional groups formed from the oxygen radicals contribute to raise up an affinity of VGCF to matrix or another VGCF, VGCF having such functional groups can agglomerate together and molded members of VGCF and composite members of VGCF can be formed with high packing density, good shape retentivity, high impact strength and high thermal and electrical conductivity.

[0047] On the other hand, when the carbon fibers are fractured after the graphitization of the vapor-grown carbon fibers in accordance with the process of the present invention, the effects to be achieved by the present invention can be created because there exist a large number of functional groups on the fracture surfaces of the carbon fibers, which can work effectively with the matrix or the binder so that the VGCF are provided with a sufficient degree of wettability with the matrix or the binder.

c. Molded Members And Composite Members

[0048] The molded members according to the present invention consist solely or substantially solely of the VGCF as described hereinabove. The molded members may contain a binder capable of binding the VGCF together in such an amount as failing to adversely affect the objects of the present invention. The amount of the binder may be usually less than 20% by weight. The molded members can be formed and processed by molding or forming processes, for example, by hydrostatic pressure-isotropic pressure molding techniques, hot press method or cast film process with solvent.

[0049] As the molded members consist solely or substantially solely of the VGCF, all fibers of the VGCF come into contact with one another in the molded members, thereby imparting highly electrical and thermal conductivity. Further, the molded members consisting solely or substantially solely of the VGCF according to the present invention can offer the advantage that they are superior in characteristics as a carrier for a catalyst.

[0050] The vapor-grown and graphitized carbon fibers of the invention can be used for a negative electrode of a

lithium ion secondary battery.

[0051] As the composite members according to the present invention, there may be mentioned, for example, composite materials and composite molded members, each consisting of the VGCF according to the present invention and the matrix.

[0052] The composite materials may include, for example, those which have the VGCF according to the present invention dispersed in a matrix such as a thermosetting resin and a thermoplastic resin. The composite molded members may include, for example, those which are molded members consisting of the VGCF according to the present invention and the matrix. As the matrix to be used for the composite materials, there may be mentioned, for example, a resin such as a thermosetting resin, a thermoplastic resin, a metal, a rubber material, an adhesive composition or a paint composition. As the matrix to be used for the composite molded members, there may be used, for example, a resin, a metal or a rubbery material. The quantity of the VGCF according to the present invention to be used for the composite materials or the composite molded members may be usually 50% by weight or more with respect to the total weight of the composite members. As the composite materials can impart good properties to the molded state of the molded products and they can be densely packed at high VGCF proportion, the products such as paints and adhesives can provide the resulting film with a high physical strength, high electrical conductivity, and a high thermal conductivity. The composite molded members can offer excellent processing characteristics so that their processed surfaces are provided with beautiful finish, in addition to the other physical characteristics that can be achieved by the composite materials. Hence, the composite members according to the present invention, such as the composite materials and the composite molded members, can be used as a high electrically and thermally conductive material and as a carrier for a catalyst.

[0053] The present invention will be described more in detail by way of examples. It should be understood herein that the present invention should not be interpreted in any respect to be limited to the examples as will be described hereinafter.

Example 1:

[0054] Vapor-grown carbon fibers having a mean fiber diameter of 0.8 μm , a mean fiber length of 132 μm and a mean aspect ratio of 165 were placed in an atmosphere in which argon gas is filled, and the carbon fibers were subjected to graphitization at 2,800°C for 30 minutes. Thereafter, the resulting pre-VGCF were fractured by applying a high impact at 8,000 rpm (peripheral speed: 100 meters per second) for 2 minutes with a high-impact treatment apparatus or a hybridizer (Model: NHS-1; K.K. Nara Kikai Seisakusho) while flowing gas at a high speed. After the fracture treatment has been finished, 100 fibers were chosen in a random way and they were observed with a scanning electron microscope. As a result of the observation with the scanning electron microscope, it has been found that they had a mean fiber diameter of 0.8 μm , a mean fiber length of 8.4 μm , and a mean aspect ratio of 10.5. The fibers were then measured for spin density in a magnetic field sweep range of 325.4 ± 25 mT with an electron resonance measurement device (Model: JES-FE 3XG; Nippon Denshi K.K.). As a result, it was found that the fibers had an absorption peak at a spin density of 6.2×10^{18} spins/g at $g=2.015$. When the treatment by the fracture continued for 40 minutes, the absorption peak was reduced to a spin density of 1.6×10^{18} spins/g.

[0055] After the pre-VGCF were subjected to the fracturing treatment for 2 minutes, they were mixed with a mixture of a phenol resin with methanol so as to account for 60% by weight, 70% by weight, and 80% by weight, respectively, when translated into the percentage by weight after vaporization of methanol. Thereafter, bubbles present in the resulting mixture were removed and the mixture was coated on a glass plate, followed by drying it at 80 °C for 10 minutes and then at 150 °C for 10 minutes to vaporize methanol and to become set. Then, the appearance of the coating was observed and the surface resistance thereof was measured. The results are shown in Table 1 below.

TABLE 1

Proportion of Carbon Fibers (% by weight)	Surface Resistance (Ω)	State of Coating
60	4.3	⊙
70	3.8	○
80	7.3	○
Notes:		
"⊙" - State of coating sustained, high strength, and smooth surface		
"○" - State of coating sustained, and ready for use.		

Comparative Example 1:

[0056] Vapor-grown carbon fibers having a mean fiber diameter of 0.8 μm , a mean fiber length of 132 μm and a mean aspect ratio of 165 were fractured by applying a high impact at 8,000 rpm for 2 minutes with a high-impact treatment apparatus or a hybridizer (Model: NHS-1; K.K. Nara Kikai Seisakusho), and the fractured carbon fibers were then placed in an atmosphere in which argon gas is filled and subjected to graphitization at 2,800 °C for 30 minutes. The resulting carbon fibers had a mean aspect ratio of 12. The resulting vapor-grown and graphitized carbon fibers were then measured for spin density in the same manner as in Example 1. As a result, it was found that the fibers had an absorption peak at a spin density of 9.3×10^{18} spins/g at $g=2.015$. When the fracturing treatment was continued for 40 minutes, it was not found that the spin density was decreased to a large extent. Thereafter, the vapor-grown and graphitized carbon fibers were treated in substantially the same manner as in Example 1. The results are shown in Table 2 below.

TABLE 2

Proportion of Carbon Fibers (% by weight)	Surface Resistance (Ω)	State of Coating
60	11.2	○
70	17.2	△
80	Not measurable	×
Notes:		
"○" - Form of coating sustained, and ready for use.		
"△" - Form of coating sustained, yet the surface of the coating may break upon some operations		
"×" - No form of coating sustained, the coating may break upon touch		

Example 2:

[0057] Vapor-grown carbon fibers having a mean fiber diameter of 1.3 μm , a mean fiber length of 110 μm and a mean aspect ratio of 84.6 were placed in an atmosphere in which argon gas is filled, and the vapor-grown carbon fibers were subjected to graphitization at 2,500°C for 20 minutes. Thereafter, the resulting pre-VGCF were fractured by applying a high impact at 7,200 rpm (peripheral speed: 90 meters per second) for 2 minutes with the high-impact treatment apparatus while flowing gas at a high speed. After the fracture treatment has been finished, 100 fibers were chosen in a random way and they were observed with a scanning electron microscope. As a result of the observation with the scanning electron microscope, it has been found that they had a mean fiber diameter of 1.3 μm , a mean fiber length of 20 μm , a mean aspect ratio of 15.4, and a spin density of 5.9×10^{18} spins/g at $g=2.015$. Thereafter, the VGCF were mixed with a polyethylene fine powder so as to account for 0.5% by weight and 10% by weight. The resulting mixture was packed into a rubber tube having an inner diameter of 25 mm and a length of 60 mm and the rubber tube was pressurized at 7,000 kg/cm² with a pressurizing machine (Model: BIP; Nikkiso K.K.) to form a molded member. The molded member was measured for its apparent density and the appearance of the molded member was observed. The results are shown in Table 3 below.

TABLE 3

Proportion of Binding Material (% by weight)	Apparent Density	State of Coating
0	1.54	○
5	1.79	⊙
10	1.84	⊙
Notes:		
"⊙" - State of coating sustained, high strength, and smooth surface		
"○" - State of coating sustained, and ready for use.		

Comparative Example 2:

[0058] The procedures in Example 2 were followed in the same manner, except for fracturing the pre-VGCF at a high impact while flowing gas at a high speed and then graphitizing it. The results are shown in Table 4 below. The resulting VGCF had a mean aspect ratio of 17 and a spin density of 9.1×10^{18} spins/g.

TABLE 4

Proportion of Binding Material (% by weight)	Apparent Density	State of Coating
0	1.16	Δ
5	1.22	Δ
10	1.45	○
Notes: "○" - State of coating sustained, and ready for use "Δ" - State of coating sustained, yet the surface of the coating may break upon operations		

Comparative Example 3:

[0059] The procedures in Example 2 were followed in the same manner, except for fracturing the vapor-grown carbon fibers at 2,000 rpm (a peripheral speed: 25 meters per second) while flowing gas at a high speed and then graphitizing it. The resulting VGCF had a mean aspect ratio of 53 and a spin density of 9.3×10^{18} spins/g. The results are shown in Table 5 below.

TABLE 5

Proportion of Binding Material (% by weight)	Apparent Density	State of Coating
0	-	×
5	-	×
10	1.26	Δ
Notes: "Δ" - State of coating sustained, yet the surface of the coating may break upon operation "×" - No shape formed and coating may break upon touch		

Example 3:

[0060] Carbon fibers grown in the vapor phase by the flow method and having a mean fiber diameter of $2.3 \mu\text{m}$ and a mean fiber length of $200 \mu\text{m}$ or larger were graphitized at $2,800^\circ\text{C}$ in argon gas. The resulting vapor-grown and graphitized carbon fibers were charged in the hybridizer and fractured at 8,000 rpm for 3 minutes. As a result, there were prepared the grown-in-the-vapor-phase and graphitized carbon fibers having a mean fiber diameter of $2.2 \mu\text{m}$, a mean fiber length of $14.6 \mu\text{m}$, and a spin density of 3.7×10^{18} spins/g at $g=2.015$.

[0061] On the other hand, a solution was prepared by placing 0.05 gram of polyvinylidene fluoride in an agate mortar and admixing it with 0.5 ml of 1-methyl-2-pyrrolidone.

[0062] To the resulting solution were added 0.95 gram of the grown-in-the-vapor-phase and graphitized carbon fibers prepared hereinabove and the mixture was stirred well to give a paste.

[0063] Then, an electrode was prepared by coating the resulting paste on the top of 10 mm x 40 mm nickel mesh washed well with acetone so as to cover its area of 10 mm x 10 mm surface of the nickel mesh, followed by drying the coating at 100°C for 23 hours in vacuo.

[0064] A three-electrode cell was assembled with the resulting electrode in a glove box having an atmosphere in which oxygen and water content were replaced sufficiently with argon gas. As the counter electrode and the reference electrode, there were used each a 10 mm x 40 mm x 2 mm metallic lithium. Further, as an electrolyte, there was used a solution prepared by dissolving LiClO_4 in a 1:1 mixture of ethylene carbonate and diethyl carbonate so as to have LiClO_4 contained at the concentration of 1 mole per liter.

[0065] Each of the electrodes was connected with a charge-discharge unit and allowed to stand until the voltage became constant. Thereafter, the charge and the discharge cycles between 0 V and 2.5 V of potential difference between the working electrode and the reference electrode were repeated. The results up to three cycles are shown in Table 6 below.

Comparative Example 4:

[0066] Carbon fibers having a mean fiber diameter of $2.3 \mu\text{m}$ and a mean fiber length of $200 \mu\text{m}$ or larger grown in the vapor phase by the flow method were fractured with the hybridizer at 8,000 rpm for 3 minutes to thereby yield the

carbon fibers, followed by carrying out the graphitization by heating the carbon fibers at 2,800 °C in argon gas. The resulting carbon fibers were found to have a mean fiber diameter of 2.2 µm, a mean fiber length of 18.3 µm, and a spin density of 9.3×10^{18} spins/g at $g=2.015$. The grown-in-the-vapor-phase and graphitized carbon fibers were then formed into a three-electrode cell in the same manner as in Example 3. Table 6 below indicates the results up to three repetitions.

TABLE 6

	NO. OF CYCLES	CHARGE AMOUNT (mAh/g)	DISCHARGE AMOUNT (mAh/g)	COULOMB EFFICIENCY(%)
EXAMPLE 3	1	460	385	84
	2	398	375	94
	3	390	370	95
COMPARATIVE EXAMPLE 4	1	362	235	65
	2	311	227	73
	3	275	220	81

[0067] The VGCF according to the present invention are suitable for the preparation of composite members such as composite materials, which are compounded at a high packing density with a material such as a plastic material, a rubbery material, a metallic material, a ceramic material, a paint composition or an adhesive composition, and composite molded members consisting solely or substantially solely of the VGCF fractured in accordance with the present invention, which may contain a small amount of a binding material.

[0068] The process for the preparation of the VGCF according to the present invention comprises subjecting the carbon fibers grown in the vapor phase to graphitization and then fracturing them by applying a high impact thereto, thereby providing the VGCF with the fracture plane having a less amount of oxygen radicals.

[0069] The molded members according to the present invention consist solely or substantially solely of the VGCF so that the VGCF can be in contact with one another to such a sufficient extent that they are provided with remarkably high electrical and thermal conductivity. They can also be used appropriately as a carrier for a catalyst. The molded members are excellent for use as an electrode for lithium ion secondary battery in which lithium forms intercalation with carbon.

[0070] The composite members according to the present invention can impart a good state to their molded products and contain the VGCF at a high packing density. When the composite members according to the present invention are used as a paint or an adhesive, the resulting film can give a highly strong film and a highly electrically and thermally conductive film. When the composite members are formed into the molded members, the resulting molded members can demonstrate superior working characteristics e.g. their finished surfaces will be beautiful after they are worked, in addition to those properties as described hereinabove.

[0071] Hence, the molded members and the composite members according to the present invention can be employed as a material having a high degree of electrical and thermal conductivity and as a carrier for a catalyst.

Claims

- Carbon fibers grown at 800-1300°C in a vapor phase, graphitized and then fractured, having a mean fiber diameter of 5 µm or smaller, a mean fiber length of 90 µm or shorter, a mean aspect ratio of from 1 to 18, obtainable by application of high impact energy in a fracturing device for a time sufficient to reduce the spin density, measured at $g=2.015$, to a value of 8×10^{18} spins/g or less when measured by the electron spin resonance absorption method, said carbon fibers having a morphology which has the appearance of the annual growth rings of a tree.
- Vapor-grown and graphitized carbon fibers as claimed in claim 1, where said vapor-grown and graphitized carbon fibers have a mean fiber diameter ranging from 0.1 µm to 3 µm.
- Vapor-grown and graphitized carbon fibers as claimed in claim 1, where said vapor-grown and graphitized carbon fibers have a mean fiber diameter ranging from 0.3 µm to 2 µm.
- Vapor-grown and graphitized carbon fibers as claimed in claim 1, where said vapor-grown and graphitized carbon

fibers have an aspect ratio of from 2 to 16.

5. Vapor-grown and graphitized carbon fibers as claimed in claim 1, where said vapor-grown and graphitized carbon fibers have an aspect ratio of from 5 to 15.
6. Vapor-grown and graphitized carbon fibers as claimed in claim 1, where said vapor-grown and graphitized carbon fibers have an interplanar distance (d_{002}) of a graphite lattice of 3.45 Å or less.
7. Vapor-grown and graphitized carbon fibers as claimed in claim 1, where said vapor-grown and graphitized carbon fibers have an interplanar distance (d_{002}) of a graphite lattice of from 3.35 Å to 3.42 Å.
8. Vapor-grown and graphitized carbon fibers as claimed in claim 1, where said vapor-grown and graphitized carbon fibers have an interplanar distance (d_{002}) of a graphite lattice of from 3.35 Å to 3.37 Å.
9. Vapor-grown and graphitized carbon fibers as claimed in claim 1, where said vapor-grown and graphitized carbon fibers have a thickness (L_c) of a laminated lattices in a crystal of 30 Å or thicker.
10. Vapor-grown and graphitized carbon fibers as claimed in claim 1, where said vapor-grown and graphitized carbon fibers have a thickness (L_c) of a laminated lattices in a crystal of 300 Å or thicker.
11. Vapor-grown and graphitized carbon fibers as claimed in claim 1, where said vapor-grown and graphitized carbon fibers have a thickness (L_c) of a laminated lattices in a crystal of 1,000 Å or thicker.
12. A process for the preparation of vapor-grown and graphitized carbon fibers as claimed in claim 1, comprising: subjecting substantially non-fractured carbon fibers grown in a vapor phase to graphitization at temperature of 2,000°C or higher and then subjecting the resulting vapor-grown and graphitized carbon fibers to fracture treatment by applying a high impact so as to have a spin density of 8×10^{18} spins/g or less, when measured by the electron spin resonance absorption method.
13. A process for the preparation of vapor-grown and graphitized carbon fibers as claimed in claim 12, wherein said fracture treatment is carried out with a high-impact treatment apparatus comprising a cylindrical container having a plurality of impact blades so arranged radially as to be rotatable and a self-circulation pathway serving as a passage of flow, so arranged as to connect an peripherally outer side wall of said cylindrical container with a central portion of a flat plate surface of said cylindrical container.
14. A process for the preparation of vapor-grown and graphitized carbon fibers as claimed in claim 13, wherein said impact blades are rotated at 40 meters per second or higher.
15. A molded member consisting substantially of vapor-grown and graphitized carbon fibers as claimed in claim 1.
16. A molded member as claimed in claim 15, wherein said molded member has a mean fiber diameter of from 1.5 μm to 3.0 μm .
17. A composite member comprising vapor-grown and graphitized carbon fibers as claimed in claim 1, and a matrix.
18. A composite member as claimed in claim 17, wherein said vapor-grown and graphitized carbon fibers are contained in a proportion of 50% by weight or more.
19. A secondary battery having a negative electrode with an anode active material, characterized in that said anode active material comprises vapor-grown and graphitized carbon fibers as claimed in any one of claims 1 to 11.

Patentanspruch

1. Kohlenstoffasern, welche bei 800 bis 1300 °C in einer Dampfphase gezüchtet, graphitisiert und dann gebrochen bzw. frakturiert sind, mit einem durchschnittlichen Faserdurchmesser von 5 μm oder weniger, einer mittleren Faserlänge von 90 μm oder weniger, einem mittleren Längenverhältnis bzw. Seitenverhältnis von 1 bis 18, erhältlich durch Aufbringung einer hohen Stoßenergie in einer Frakturierungsvorrichtung über eine Zeit, welche zur Ver-

gerung der Spindichte, gemessen bei $g=2,015$, auf einen Wert von 8×10^{18} spin/g oder weniger bei Messung mittels der Elektronenspin-Resonanzabsorptionsmethode ausreicht, wobei die Kohlenstoffasern eine Morphologie aufweisen, welche das Erscheinungsbild der Jahresringe eines Baumes besitzt.

- 5 2. Dampfgezüchtete und graphitisierte Kohlenstofffasern nach Anspruch 1, wobei die dampfgezüchteten und graphitisierten Kohlenstofffasern einen mittleren Faserdurchmesser im Bereich von $0,1 \mu\text{m}$ bis $3 \mu\text{m}$ aufweisen.
3. Dampfgezüchtete und graphitisierte Kohlenstofffasern nach Anspruch 1, wobei die dampfgezüchteten und graphitisierten Kohlenstofffasern einen mittleren Faserdurchmesser im Bereich von $0,3 \mu\text{m}$ bis $2 \mu\text{m}$ aufweisen.
- 10 4. Dampfgezüchtete und graphitisierte Kohlenstofffasern nach Anspruch 1, wobei die dampfgezüchteten und graphitisierten Kohlenstofffasern ein Längenverhältnis von 2 bis 16 aufweisen.
- 15 5. Dampfgezüchtete und graphitisierte Kohlenstofffasern nach Anspruch 1, wobei die dampfgezüchteten und graphitisierten Kohlenstofffasern ein Längenverhältnis von 5 bis 15 aufweisen.
6. Dampfgezüchtete und graphitisierte Kohlenstofffasern nach Anspruch 1, wobei die dampfgezüchteten und graphitisierten Kohlenstofffasern einen Zwischenebenenabstand (d_{002}) eines Kohlenstoffgitters von $3,45 \text{ \AA}$ oder weniger aufweisen.
- 20 7. Dampfgezüchtete und graphitisierte Kohlenstofffasern nach Anspruch 1, wobei die dampfgezüchteten und graphitisierten Kohlenstofffasern einen Zwischenebenenabstand (d_{002}) eines Kohlenstoffgitters von $3,35 \text{ \AA}$ bis $3,42 \text{ \AA}$ aufweisen.
- 25 8. Dampfgezüchtete und graphitisierte Kohlenstofffasern nach Anspruch 1, wobei die dampfgezüchteten und graphitisierten Kohlenstofffasern einen Zwischenebenenabstand (d_{002}) eines Kohlenstoffgitters von $3,35 \text{ \AA}$ bis $3,37 \text{ \AA}$ aufweisen.
- 30 9. Dampfgezüchtete und graphitisierte Kohlenstofffasern nach Anspruch 1, wobei die dampfgezüchteten und graphitisierten Kohlenstofffasern eine Dicke (L_c) eines laminierten Gitters bzw. laminierter Gitter in einem Kristall von 30 \AA oder mehr aufweisen.
10. Dampfgezüchtete und graphitisierte Kohlenstofffasern nach Anspruch 1, wobei die dampfgezüchteten und graphitisierten Kohlenstofffasern eine Dicke (L_c) eines laminierten Gitters bzw. laminierter Gitter in einem Kristall von 300 \AA oder mehr aufweisen.
- 35 11. Dampfgezüchtete und graphitisierte Kohlenstofffasern nach Anspruch 1, wobei die dampfgezüchteten und graphitisierten Kohlenstofffasern eine Dicke (L_c) eines laminierten Gitters bzw. laminierter Gitter in einem Kristall von 1000 \AA oder mehr aufweisen.
- 40 12. Verfahren zur Herstellung von dampfgezüchteten und graphitisierten Kohlenstofffasern nach Anspruch 1, mit folgenden Schritten: Aussetzung im wesentlichen nicht frakturierter, in einer Dampfphase gezüchteter Kohlenstofffasern einer Graphitisierung bei einer Temperatur von 2000°C oder mehr, und dann Aussetzung der sich ergebenden dampfgezüchteten und graphitisierten Kohlenstofffasern einer Frakturbehandlung durch Aufbringung eines starken Stoßes, so daß sich eine Spindichte von 8×10^{18} spin/g oder weniger ergibt, dies gemessen mit der Elektronenspin-Resonanzabsorptionsmethode.
- 45 13. Verfahren zur Herstellung dampfgezüchteter und graphitisierter Kohlenstofffasern nach Anspruch 12, wobei die Frakturbehandlung innerhalb einer Vorrichtung zur Behandlung mit starken Stößen bzw. zur High-Impact-Behandlung durchgeführt wird, welche einen zylindrischen Behälter mit einer Anzahl von Auftreff- bzw. Stoßklingen, die derart radial angeordnet sind, daß sie drehbar sind, und einen Selbstzirkulationsweg, der als Fließdurchgang dient und derart angeordnet ist, daß er eine peripher äußere Seitenwand des zylindrischen Behälters mit einem mittleren Abschnitt einer Stirnfläche des zylindrischen Behälters verbindet, aufweist.
- 50 14. Verfahren zur Erstellung von dampfgezüchteten und graphitisierten Kohlenstofffasern nach Anspruch 13, wobei die Stoßklingen mit einer Geschwindigkeit von 40 Metern pro Sekunde oder mehr gedreht werden.
- 55 15. Geformtes Element, im wesentlichen bestehend aus Dampfgezüchteten und graphitisierten Kohlenstofffasern

nach Anspruch 1.

16. Geformtes Element nach Anspruch 15, wobei das geformte Element einen mittleren Faserdurchmesser von 1,5 μm bis 3,0 μm aufweist.
17. Verbundelement mit dampfgezüchteten und graphitisierten Kohlenstofffasern nach Anspruch 1 und einer Matrix.
18. Verbundelement nach Anspruch 17, wobei die Dampfgezüchteten und graphitisierten Kohlenstofffasern in einem Verhältnis von 50 Gewichtsprozent oder mehr vorliegen.
19. Sekundärbatterie mit einer negativen Elektrode mit einem anodenaktiven Material, dadurch gekennzeichnet, daß das anodenaktive Material dampfgezüchtete und graphitisierte Kohlenstofffasern nach einem der Ansprüche 1 bis 11 aufweist.

Revendications

1. Fibres de carbone ayant eu une croissance à 800 - 1300°C en phase vapeur, une graphitisation puis une fracturation, ayant un diamètre moyen des fibres de 5 μm ou moins, une longueur moyenne des fibres de 90 μm ou moins, un rapport d'aspect moyen de 1 à 18, pouvant être obtenues par application d'une forte énergie d'impact dans un dispositif de fracturation pendant un temps suffisant pour réduire la densité de spins, mesurée à $g = 2,015$, à une valeur de 8×10^{18} spins/g ou moins, la mesure étant effectuée par une méthode d'absorption par résonance de spin électronique, lesdites fibres de carbone ayant une morphologie qui présente l'aspect des anneaux de croissance annuels d'un arbre.
2. Fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, dans lesquelles lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ont un diamètre moyen des fibres compris entre 0,1 et 3 μm .
3. Fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, dans lesquelles lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ont un diamètre moyen des fibres compris entre 0,3 et 2 μm .
4. Fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, dans lesquelles lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ont un rapport d'aspect de 2 à 16.
5. Fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, dans lesquelles lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ont un rapport d'aspect de 5 à 15.
6. Fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, dans lesquelles lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ont une distance entre plans réticulaires (d_{002}) d'un réseau de graphite de 3,45 Å ou moins.
7. Fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, dans lesquelles lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ont une distance entre plans réticulaires (d_{002}) d'un réseau de graphite de 3,35 à 3,42 Å.
8. Fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, dans lesquelles lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ont une distance entre plans réticulaires (d_{002}) d'un réseau de graphite de 3,35 à 3,37 Å.
9. Fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, dans lesquelles lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ont une épaisseur (L_c) d'un réseau feuilleté dans un cristal, d'au moins 30 Å ou plus.
10. Fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, dans

lesquelles lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ont une épaisseur (L_c) d'un réseau feuilleté dans un cristal, de 300 Å ou plus.

11. Fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, dans lesquelles lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ont une épaisseur (L_c) d'un réseau feuilleté dans un cristal, de 1000 Å ou plus.

12. Procédé de préparation de fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, qui comprend les étapes consistant à soumettre des fibres de carbone essentiellement non fracturées, ayant eu une croissance en phase vapeur, à une graphitisation à une température de 2000°C ou plus, puis à soumettre les fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation ainsi obtenues à un traitement de fracture par application d'une grande énergie d'impact de façon à arriver à une densité de spins de 8×10^{18} spins/g ou moins, la mesure utilisant une méthode d'absorption par résonance de spin électronique.

13. Procédé de préparation de fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 12, dans lequel ledit traitement de fracture est réalisé à l'aide d'un appareil de traitement assurant un impact élevé, comprenant un récipient cylindrique ayant une pluralité de pales d'impact, disposées radialement de façon à pouvoir tourner, et un chemin d'auto-circulation servant de passage pour l'écoulement, disposé de façon à relier une paroi latérale extérieure périphérique dudit récipient cylindrique à une portion centrale d'une surface de type plaque plate dudit récipient cylindrique.

14. Procédé de préparation de fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 13, dans lequel lesdites pales d'impact tournent à raison de 40 mètres par seconde ou plus.

15. Objet moulé, constitué essentiellement de fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1.

16. Objet moulé selon la revendication 15, dans lequel ledit objet moulé a un diamètre moyen des fibres de 1,5 à 3,0 µm.

17. Objet composite, comprenant des fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon la revendication 1, et une matrice.

18. Objet composite selon la revendication 17, dans lequel lesdites fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation sont présentes selon une proportion de 50 % en poids ou plus.

19. Batterie secondaire ayant une électrode négative avec une matière active d'anode, caractérisée en ce que ladite matière active d'anode comprend des fibres de carbone ayant eu une croissance en phase vapeur et une graphitisation selon l'une quelconque des revendications 1 à 11.

F I G . 1

